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ORDERED MAGNETIC FRUSTRATION:
X. MAGNETIC STRUCTURE OF α-$KCrF_4$ AT 1.5 K

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The magnetic structure of orthorhombic α-$KCrF_4$ at 1.5 K (S.G. Pnma, $a = 15.76$ Å, $b = 7.43$ Å, $c = 18.38$ Å, $Z = 24$) was solved from powder neutron diffraction data. Magnetic constraints, due to antiferromagnetic coupling inside the triangular cycles of $Cr^{3+}F_6$ corner sharing octahedra, lead approximately to a star configuration of moments in the (010) plane ($\mu_{Cr1} = 2.11(11)\mu_B$, $\mu_{Cr2} = 1.91(12)\mu_B$, $\mu_{Cr3} = 2.19(6)\mu_B$). The magnetic coupling between Cr^{3+} along [010], which corresponds to the direction of infinite columns, is strictly antiferromagnetic.

1. Introduction

Experimental examples of magnetic frustration [1] are still rather scarce [2–11]. Among them, the most common case is provided by the triangular plane lattice with antiferromagnetic interactions, which has also been extensively studied, from a theoretical point of view (see for example refs. [12–15] and references therein). This geometry leads to three antiferromagnetic sublattices oriented at 120° to each other.

α-$KCrF_4$, first isolated by de Kozak [16], provides an interesting example for the study of frustration. Dewan and Edwards solved its crystal structure [17,18] using an orthorhombic unit cell (S.G. Pnma, $a = 15.76$ Å, $b = 7.43$ Å, $c = 18.38$ Å, $Z = 24$). It is built up from isolated infinite triangular columns of corner sharing CrF_6 octahedra (fig. 1) between which K^+ ions are inserted.

Within the isolated columns, the Cr^{3+} sublattice, submitted to d^3–d^3 180° antiferromagnetic superexchange interactions, is trigonal prismatic. Therefore it involves both frustrating triangular (within the (010) plane) and non-frustrating square platelets of nearest neighbours. This must lead to a quasi-1D frustrated magnetic behaviour below the Néel temperature $T_N = 4(1)$ K [19,20]. In this paper, we present the magnetic structure of α-$KCrF_4$ and compare the results with those obtained on HTB-FeF_3 [3] in which the trigonal prisms share edges and form a 3D magnetic sublattice.

2. Experimental

The powdered sample was obtained from a stoichiometric mixture of elementary fluorides, heated at 700°C for 24 h in gold tubes sealed under argon. The neutron diffraction patterns at 5 and 1.5 K were collected on the high-flux powder diffractometer D1B of the Institut Laue–Langevin at Grenoble, using a wavelength of 2.518 Å. The powdered sample was contained in a vanadium can ($\phi = 10$ mm, $h = 50$ mm) held in a standard helium cryostat. Two patterns were recorded below and above the Néel temperature, at 1.5 and 5 K, respectively. All refinements were performed with the Rietveld program [21,22]. The scattering lengths and magnetic form factors were taken from refs. [23] and [24], respectively.

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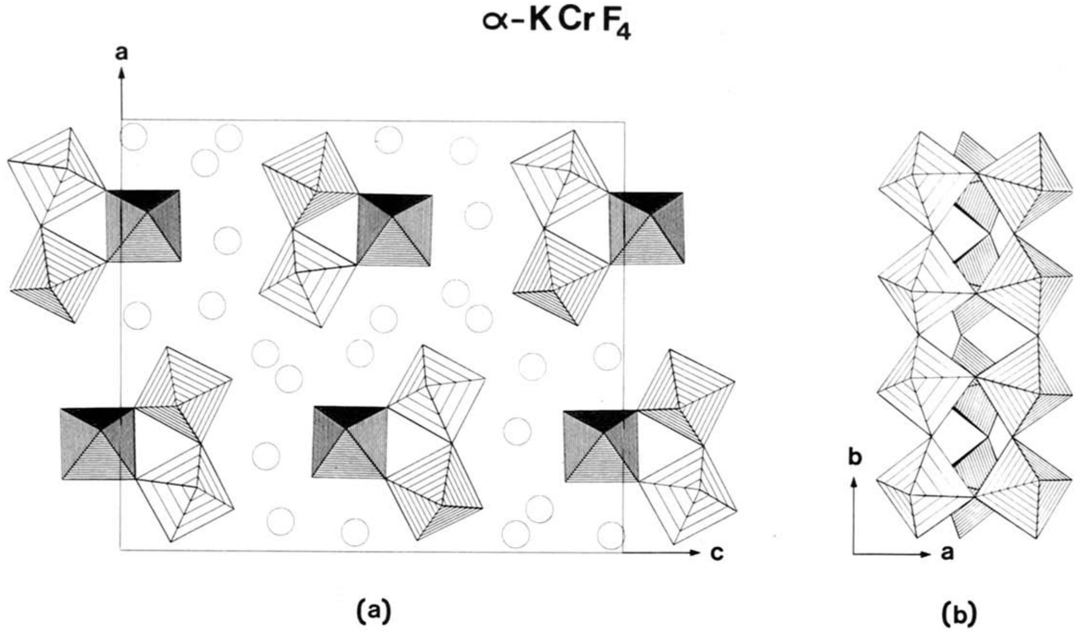

Fig. 1. Crystal structure of α-KCrF$_4$ drawn with the program STRUPLO84 (29). (a) (010) projection; (b) view of one triangular column of corner sharing CrF$_6$ octahedra. The density of hatching increases from Cr1 to Cr3. Circles = K$^+$.

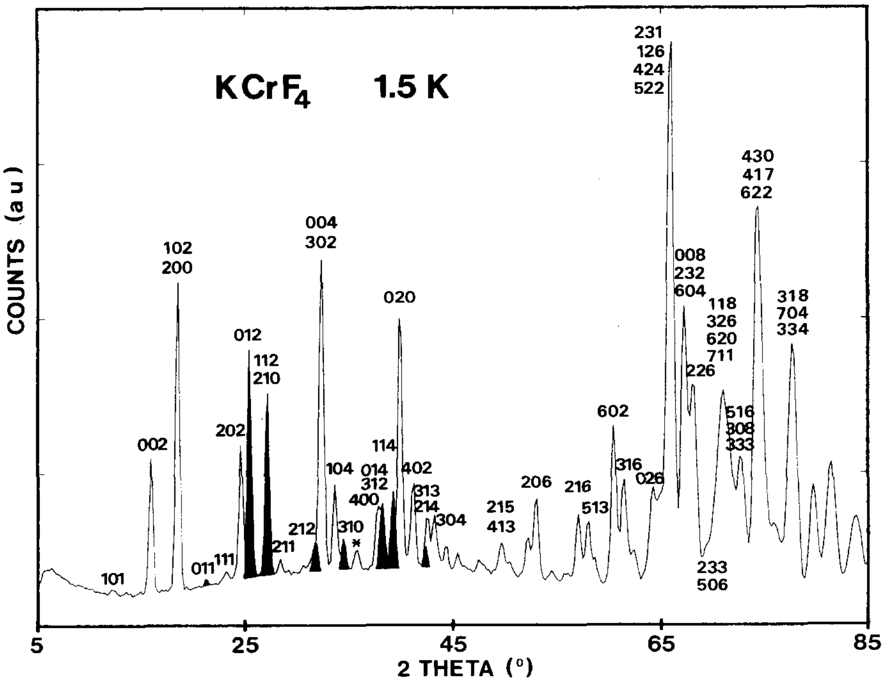

Fig. 2. Neutron diffraction pattern of α-KCrF$_4$ at 1.5 K. Purely magnetic peaks are shaded. * = impurity (CrF$_3$).

3. Magnetic structure – results and discussion

At 5 K, the compound is not yet magnetically ordered. At 1.5 K, we note an increase in some nuclear reflections and the onset of additional magnetic peaks (fig. 2). All new reflections can be indexed in the nuclear cell.

The coupling modes of KCrF$_4$ were determined by using Bertaut's macroscopic theory [25].

Let for example, $\tilde{2}_x$, $\tilde{2}_z$ and $\bar{1}$ be the three independent symmetry elements of space group Pnma. In α-KCrF$_4$ Cr^{3+} ions occupy three crystallographically different sites on the 8d general position of the space group Pnma.

Let S_i $(i = 1,8)$ be the magnetic moments of 8 Cr^{3+} on equivalent positions (table 1). We can define, on each of the three sublattices, eight base vectors, built from linear combinations of the moments, which represent the possible magnetic modes of coupling:

$$F = S_1 + S_2 + S_3 + S_4 + S_5 + S_6 + S_7 + S_8, \quad \text{(ferromagnetic mode)}$$
$$G = S_1 - S_2 + S_3 - S_4 + S_5 - S_6 + S_7 - S_8,$$
$$C = S_1 + S_2 - S_3 - S_4 + S_5 + S_6 - S_7 - S_8,$$
$$A = S_1 - S_2 - S_3 + S_4 + S_5 - S_6 - S_7 + S_8,$$
$$P = S_1 + S_2 + S_3 + S_4 - S_5 - S_6 - S_7 - S_8,$$
$$Q = S_1 - S_2 + S_3 - S_4 - S_5 + S_6 - S_7 + S_8,$$
$$R = S_1 + S_2 - S_3 - S_4 - S_5 - S_6 + S_7 + S_8,$$
$$L = S_1 - S_2 - S_3 + S_4 - S_5 + S_6 + S_7 - S_8.$$

These base vectors lead to the eight irreducible representations, given in table 2.

According to Knocke [19,20], α-KCrF$_4$ orders antiferromagnetically. All of the eight modes are compatible with this experimental result (if we reduce to zero the ferromagnetic component of the Γ_2, Γ_3 and Γ_4 modes). The calculations were carried out using the atomic positions of Dewan and Edwards [26,18]. Owing to the large number of atomic position parameters in the cell compared with the limited number of reflections available from the neutron diffraction data, we decided to refine the magnetic structure from the difference pattern 1.5–5 K. Thus, only the magnetic contribution of Cr^{3+} ions is considered. This method is a reasonable approximation owing to the small change of temperature (1.5–5 K) which does not produce any appreciable variation of the positional, thermal and cell parameters. The positional parameters of Cr^{3+} were held fixed at the (room temperature) values given by Edwards and we only refined magnetic moments on these sites. The eight possible modes were tested.

Table 1
Coordinates of magnetic ions Cr^{3+} (general position 8d) of space group Pnma

S_1	x	y	z
S_2	$\bar{x}$	$1/2+y$	$\bar{z}$
S_3	$1/2+x$	$1/2-y$	$1/2-z$
S_4	$1/2-x$	$\bar{y}$	$1/2+z$
S_5	$\bar{x}$	$\bar{y}$	$\bar{z}$
S_6	x	$1/2-y$	z
S_7	$1/2-x$	$1/2+y$	$1/2+z$
S_8	$1/2+x$	y	$1/2-z$

Table 2
Irreducible representations of Cr^{3+} in space group Pnma

Mode	x	y	z
$\Gamma_1(+++)$	G_x	C_y	A_z
$\Gamma_2(+-+)$	F_x	A_y	C_z
$\Gamma_3(-++)$	C_x	G_y	F_z
$\Gamma_4(--+)$	A_x	F_y	G_z
$\Gamma_5(++-)$	Q_x	R_y	L_z
$\Gamma_6(+--)$	P_x	L_y	R_z
$\Gamma_7(-+-)$	R_x	Q_y	P_z
$\Gamma_8(---)$	L_x	P_y	Q_z

The value of the magnetic moments was obtained by scaling the experimental nuclear diffraction profile (5 K pattern) to that calculated with the structural parameters determined by Edwards. In addition, this allowed us to verify that there was no significant variation of the structure between room temperature and 1.5 K. The best fit between observed and calculated magnetic intensities was obtained for the Γ_6 mode $P_x L_y R_z$ giving $R_\mathrm{I} = 0.037$, $R_\mathrm{wp} = 0.119$ for $2\theta < 45°$ ($R_\mathrm{I} = 0.083$, $R_\mathrm{wp} = 0.145$ for the whole pattern). Fig. 3 shows the observed and calculated profiles.

The components of magnetic moments on the cell axis are reported in table 3. The moments lie in the xOz plane. It was not possible to refine their y-component. Therefore, this component, if it exists, must be very close to zero.

The relatively low value of the moments $\approx 2\mu_\mathrm{B}$ is not unexpected, owing to the low magnetic

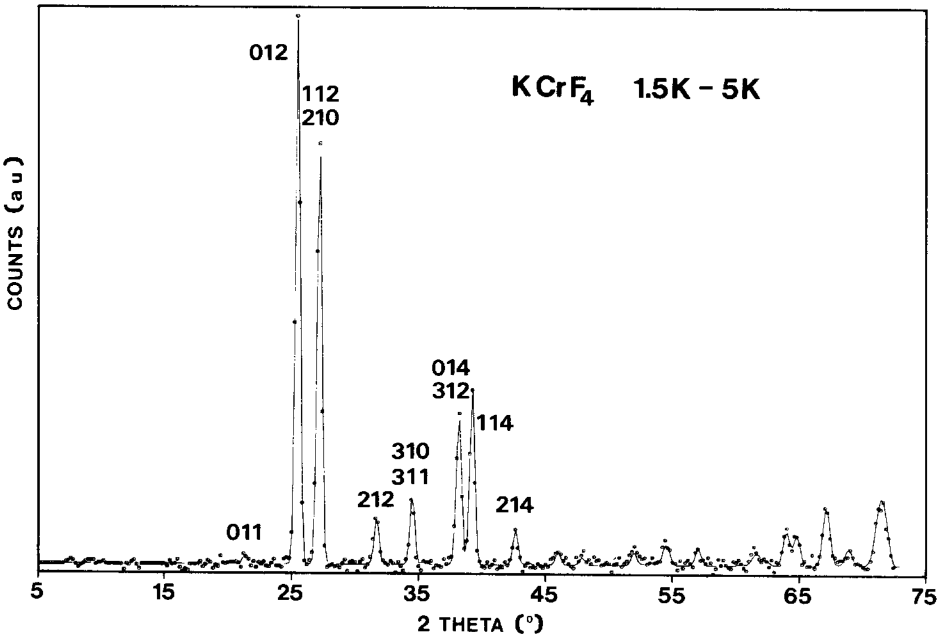

Fig. 3. Observed (·) and calculated (–) magnetic intensities (difference pattern 1.5–5 K). $2\theta < 45°$, after refinement: $R_I = 0.035$, $R_{wp} = 0.119$; whole pattern: $R_I = 0.083$, $R_{wp} = 0.145$.

ordering temperature. At 1.5 K, the magnetic saturation is not yet reached.

Magnetic dipolar energy and field calculations show that, on every Cr^{3+} site, magnetic dipolar energy is negative and that the magnetic dipolar field has roughly the same orientation as the magnetic moments (table 4).

The spin arrangement of α-$KCrF_4$ has a plane star configuration, but rather distorted from the ideal star arrangement (3 × 120°) with one small (73°) and two large angles (139° and 148°) (fig. 4). Between two consecutive planes along z, the spin coupling is strictly antiferromagnetic within each infinite column of octahedra. An analogy of spin configuration in a basic triangular arrangement can be made with other compounds such as HTB-FeF_3 (3D-antiferromagnet below $T_N = 110$ K) [3], $CsVCl_3$ [27] or $CsVI_3$ [28] (1D antiferromagnets with $T_N = 13.3$ and 32 K, respectively). They all crystallise in the hexagonal symmetry and present magnetic sublattices oriented at 120° from each other in the triangular planes. The coupling between the planes is strictly antiferromagnetic, as in α-$KCrF_4$, but in the latter the angle between the spins differs significantly from 120°. This deviation results from the difference in the crystal symmetry of these compounds. Indeed, the hexagonal symmetry of the columns in HTB-FeF_3 and $CsVX_3$ implies identical θ(M–X–M) super-exchange angles in the triangular plane and there-

Table 3
Refined magnetic moments (μ_B) in α-$KCrF_4$ at 1.5 K. Atomic positions are held fixed at their RT values [26]

Cr^{3+}	Atomic positions			Magnetic moments			
	x	y	z	M_x	M_y	M_z	M
1	0.3685	−0.0006	0.6310	−1.49 [10]	0	1.49 [5]	2.11 [11]
2	0.1357	−0.0019	0.6264	−1.69 [11]	0	−0.88 [5]	1.91 [12]
3	0.2529	−0.0009	0.4530	2.18 [5]	0	−0.17 [10]	2.19 [6]

Table 4
Magnetic dipolar energy E (j mol^{-1}) and field $H(T)$ on Cr sites in α-KCrF$_4$.

Atom	E	H_x	H_y	H_z
Cr1	−0.788	−0.1102	0	0.0552
Cr2	−0.658	−0.1085	0	−0.0462
Cr3	−0.676	0.0797	0	0.0053

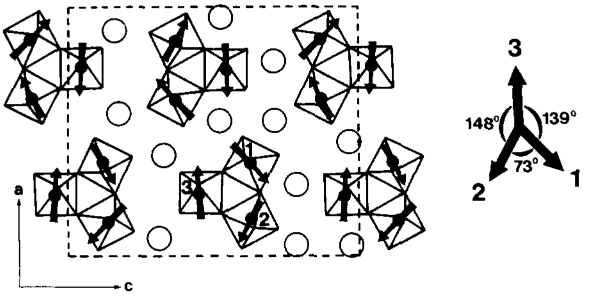

Fig. 4. Magnetic structure of α-KCrF$_4$. Moments lie in the (010) plane.

fore equal exchange integrals J between M ions thereby leading to three 120° AF sublattices. The orthorhombic symmetry of α-KCrF$_4$ provides additional degrees of freedom in the triangle and allows different M–X–M angles (fig. 5). As J_{ex} varies linearly with $\cos^2\theta$ [30], the inequality of θ implies different J_{ex} which could explain both the slightly different values of the magnetic moments of the three crystallographically different Cr^{3+} and the deviation from the ideal star configuration. The latter point was actually confirmed by a Monte Carlo simulation [31] of the ground state configuration of spins in an isolated column: using a linear J_{ex} vs. $\cos^2\theta$ relationship, the calculated spin arrangement deviates from the 120° configuration and shows one smaller and two larger angles; although the deviations from the ideal star model are smaller than observed experimentally, the trend is clearly reproduced and indicates that the departure from the ideal spin configuration originates essentially in the structural distortion of the columns.

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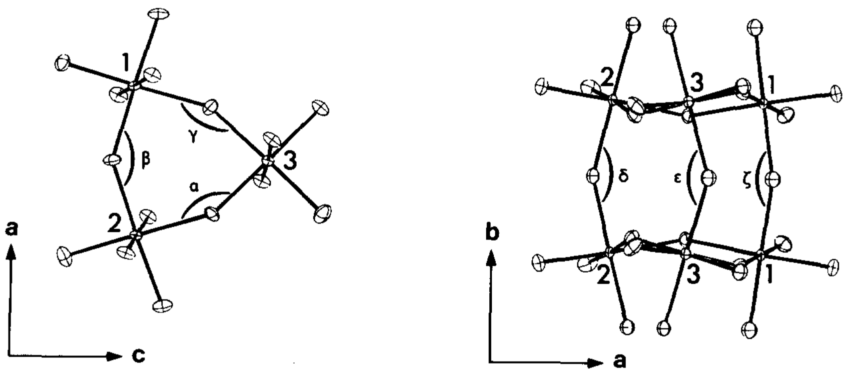

Fig. 5. Super-exchange angles θ(Cr–F–Cr) inside the column [26]. α = 144.6°, β = 140.2°, γ = 149.0°, δ = 149.9°, ε = 148.5°, ζ = 149.9°.

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